GEOCHEMISTRY OF SEDIMENT AND WATER AT TAMBRAPARNI ESTUARY, TAMIL NADU

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INDIAN INSTITUTE OF TECHNOLOGY KANPUR

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GEOCHEMISTRY OF SEDIMENT AND WATER AT TAMBRAPARNI ESTUARY, TAMIL NADU

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CERTIFICATE

It is certified that the work contained in the thesis entitled "Geochemistry of sediment and water at Tambraparni estuary, Tamil Nadu" has been carried out by G. Palanivel under my supervision and that this work has not been submitted elsewhere for a degree.

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G. Palanivel

DEDICATED

TO

MY PARENTS

&

ALL MY FRIENDS

ABSTRACT

The Tambraparni river originates in the Western Ghats and falls into the Bay of Bengal near Tuticorin in Tamil Nadu state. It has a medium sized drainage basin (5969 Sq. Km) dominated by granitoid and high grade metamorphic rocks of Archean age. This thesis summarizes geological and geochemical data collected at the estuary of the river.

According to the landform classification, the study area falls within the Eastern Coastal Plains. Sediment and Water samples were collected in the fresh water as well as the saline water zones. It was found that the bed sediment mainly contains unweathered fragments of rock forming minerals like quartz, felspar, sillimanite, garnet and pyroxene. Clay minerals are rare and occur only in bank deposits. X-ray patterns reveal poorly crystalline kaolinite and illite. It is concluded that the rate of chemical weathering is lower than the rate of mechanical weathering.

TDS, chloride and pH values in water show a general increase downstream in the estuary. Dissolved silica and phosphate show non-conservative behaviour but with contrasting trends. For example, SiO_2 values show a sharp drop from around 40 mg/l in the fresh water zone to near zero in the saline zone. Flocculation of silicate minerals by electrolytes together with biological uptake are possible factors for this trend.

In contrast, dissolved phosphate shows irregular variations between 50 to 175 μg/l with a sharp drop in the fresh water zone and later increases in the saline zone. The possible reasons are

adsorption from fresh water by sediments rich in amorphous iron oxide, desorption in saline water and interference by biological processes and pollution loading from nearby villages.

A mixed acid extraction method was developed to estimate phosphate available from sediments. Although the sediments readily released phosphate, no definite correlation was found between decrease in water and increase in sediment or the reverse.

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CHAPTER 1

INTRODUCTION AND OBJECTIVES

What happens to sediment mineralogy and water chemistry when a river meets the sea is a topic which interests scientists of various disciplines. For example, hydraulic engineers deal with problems of silting and scouring in tidal rivers. Geotechnical engineers are concerned with diagenesis and consolidation of recent marine sediments. The change in water quality and resulting effects on aquatic life is of importance to environmental engineers. Among earth scientists, geochemists are interested in calculating the river inputs to ocean system and economic geologists explore mineral and petroleum resources in near shore deposits.

Estuaries are drowned river valleys filled with diluted sea water (Berner and Berner 1987). The relative magnitudes of river flow and oceanic tidal currents control the details of estuarine circulation patterns. In a typical case, fresh to brackish water flows out as an upper layer and denser sea water moves in at the bottom. The tides vertically mix sea water with fresh water and cause significant change in water quality as well as in mineralogy of suspended sediments.

From a geochemical point of view, it is interesting to note whether the concentration of a given constituent of river water is reduced or increased during its movement in the estuary .

For this purpose, it is standard practice to select a constituent like chloride,which shows no loss or gain by interaction with sediments and then a plot is made of the variation of the given

river water constituent against increasing chloride concentration (as a measure of mixing with oceanic water). If these values lie along a straight line between the concentration in river water and the concentration in ocean water then it is classified as a "Conservative" constituent . Any deviation from this theoretical line is interpreted as "non-conservative" behavior.

From a sedimentalogical point of view, the flocculation of colloidal particles by electrolytes in sea water is an important process. This is in addition to the settling down of the coarser fraction due to the sharp velocity drop, when the river reaches the sea. Therefore, the composition of the water in the estuary together with the mineralogy of sediments represent the end stages of the derivation of dissolved and suspended load of the river by chemical weathering and mechanical disintegration of rocks in the catchment area.

Most rock forming minerals are cation aluminium silicates. They weather in the presence of dissolved CO_2 in river water to release cation, dissolved silica, and bicarbonate. There is commonly a solid residue in the form of degraded silicates like clay minerals. In specific situations a reverse weathering reactions may cause uptake of dissolved silica and other aqueous species by the suspended sediments (Raymahashay, 1971).

Reactions represented by

(1)Weathering

$$Rock+CO_2+H_2O=clay+SiO_2+cations+HCO^-_3$$

(2)Reverse Weathering

$$\text{Degraded silicates} + SiO_2 + HCO_3^- + \text{cations}$$

$$= \text{cations - Aluminium silicates} + CO_2 + H_2O$$

cause non-conservative behavior of a typical river water constituent like dissolved silica. In addition to such inorganic reactions, biological uptake combined with adsorption by sediments also causes non-conservative behavior of constituents like phosphate.

A comparison of average river and ocean compositions usually shows that in contrast with major chemicals, silica is higher in river and lower in ocean (Berner and Berner 1987). On the other hand, phosphate usually shows an initial drop at the river mouth and an increasing trend further towards the sea. Si and P being nutrient elements, it is important to confirm this trend at all estuaries.

Keeping the above literature data in mind, it was decided to verify some of the geological and geochemical aspects at the mouth of the Tambraparni river in Tamil Nadu. The Tambraparni basin has been classified as a medium size basin by Rao(1975). The report of the Institute of water studies (1986) states that the total basin area is 5969 sq.km. of which 1105 sq. km (18.5%) is hilly terrain and the rest is occupied by plains. The river originates in the Western ghats and falls into Bay of Bengal near Tuticorin (Fig. 1.1). Rao (1975) states that the river is called Tambraparni (copper water) because of the reddish colour of the bed sediments. The study of the river mouth was undertaken with the following specific objectives.

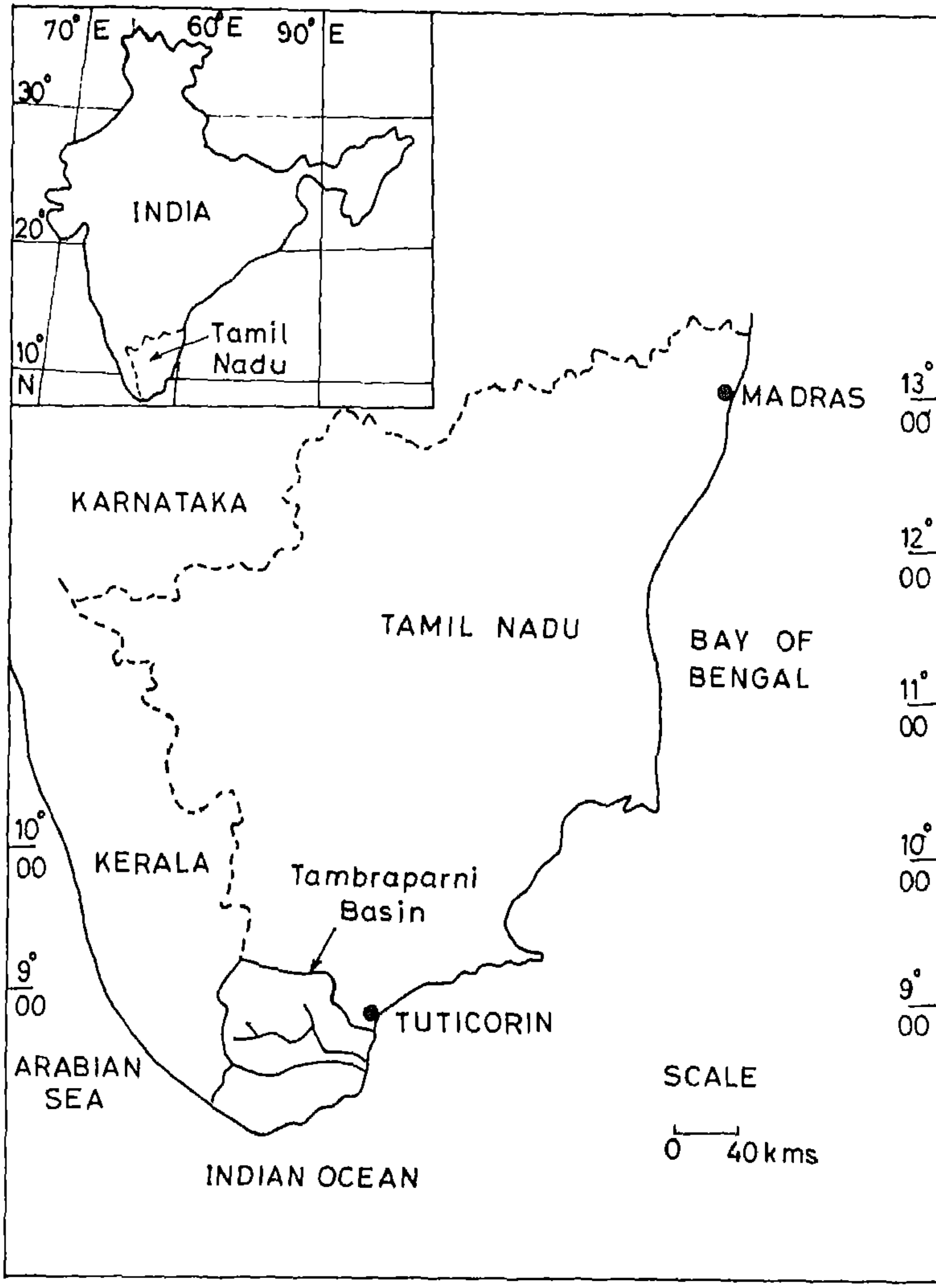


Fig.1.1: Location of Tambraparni basin

1. To compile the geology of the drainage basin and to correlate it with mineralogy of sediments transported at the river mouth.

2. To select suitable sampling points for collection of water and sediments and represent these on large scale maps prepared on the basis of field observations.

3 To demarcate the zone of estuarine mixing in terms of conductivity, TDS and chloride measurement in water.

4 To compare the variation of silica and phosphate in order to verify contrasting trends reported by earlier workers in other estuaries

5. To develop a method to estimate the phosphate content of the river sediments and establish the relationship, if any, with dissolved phosphate in river water.

CHAPTER 2

PREVIOUS WORK

2.1 Geology of Tambraparni River Basin

Distribution of rock types in this river basin has been described in detail by several workers. One of earliest investigation was by Narayanswami and Purna Lakshmi in 1967 whose results have been reproduced in Narayanswami and Purna Lakshmi (1993). These authors concentrated mainly on the Charnockitic rocks occurring in the western parts of the Tirunelveli district and adjacent Western ghats which happen to constitute the source area of the Tambraparni river. A brief description of the geology is also available from Balasubramanian et. al (1985) and Balasubramanian and Sastri (1987). According to them the entire basin is occupied by three distinct geological formations namely (1) Archean (2) Tertiary (3) recent to sub-recent. Table 2.1 gives the details of the distribution of the rocks in the basin. Around 1984-86 the Institute for water studies, Madras (1986) prepared a report based on data from GSI, CGWB, and PWD giving the geological frame work of this basin. Aerial photographs and Landsat imageries were also used in this project to demarcate the contact of various geological units and to describe structural features. According to this work the Archean formations comprised 90% of the aerial distribution of rocks within the basin. In other words the major rock types in the catchment area are charnockites, granitic gneisses, garnetiferous biotite gneiss with bands of garnetiferous sillimanite gneiss, calc gneisses, calc granulites, crystalline limestones and quartzites. The

coastal belt is occupied by Tertiary and recent sediments which occur in the form of a narrow zone parrallel to the coast line with thickness increasing towards the shore (Balasubramaniam et.al 1985). A brief description of the major rock types as given by the above authors is supplied below.

TABLE 2.1

Geological Formations in Tambraparni river basin

(From Balasubramanian and Sastry, 1987)

Age	Lithology	Distribution in the basin
Recent to sub recent	Soils, Coastal sands Red 'Teri' sands. Kankar, Tufa and Laterites, calcareous sandstones and shell limestones	eastern region adjacent to the coastline.
Tertiary	hard and compact calcareous sandstones and shell limestones	underlying the beach sands and extending up to Srivaikuntam.
	Younger granitic and Pegmatitic intrusions	
	Composite gneiss	Northeastern parts
	Granitic Mica gneiss	Central and Northern parts
Archaean	Garnetiferous mica geneiss	Southern and Southwestern parts
	Amphibolites, epidiorites and pyroxene granutites	
	Charnockites	Western and Northern parts of Tenkasi
	Crystalline limestones and Calc-granulites	Central parts around Tirunelveli and
	quartzites	Ambasamudram

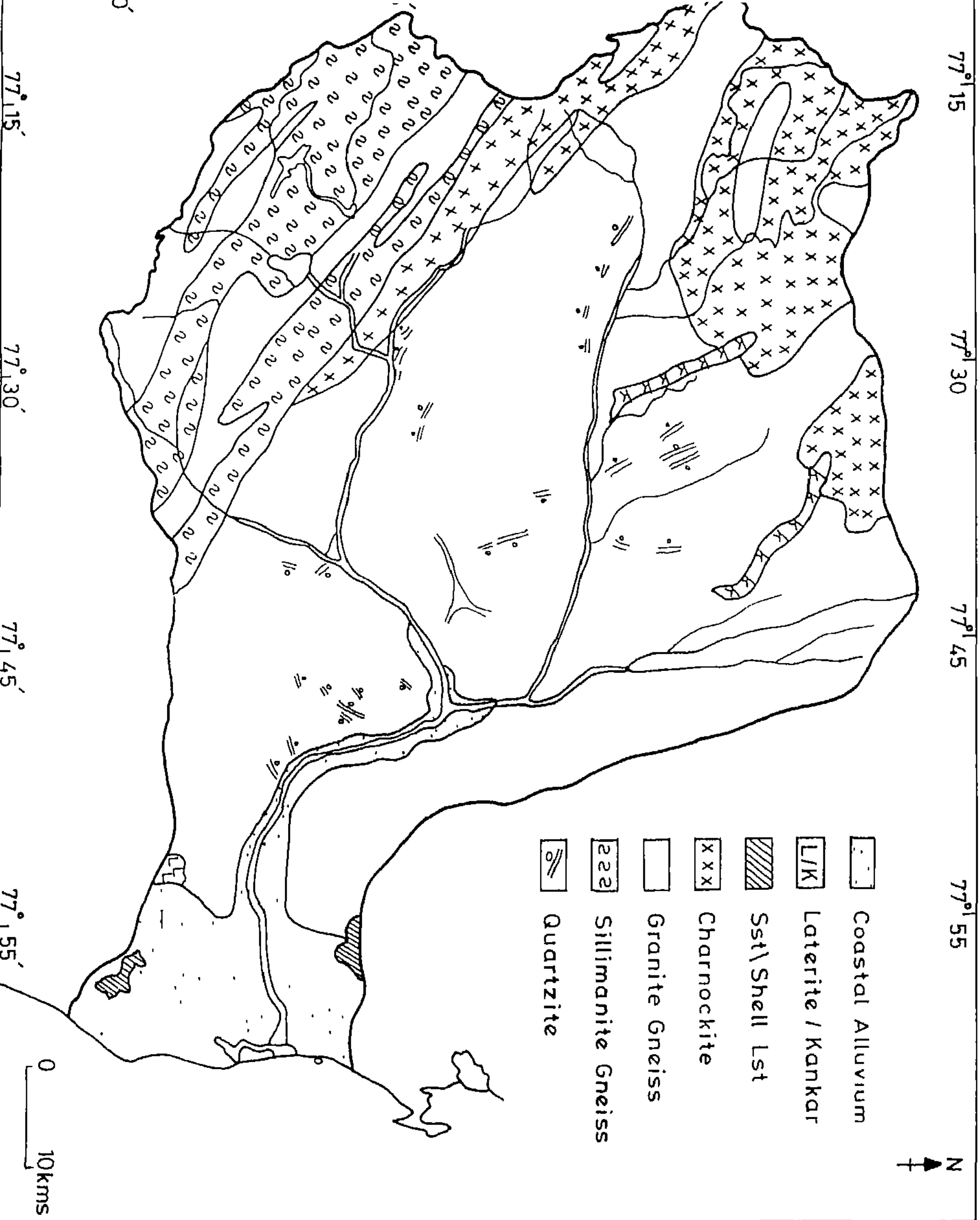


Fig.2.1. Geologic map of Tambraparni basin

1. Charnockites:

Charnockites are grey to black in colour, medium to coarse grained in texture and contain hypersthene, plagioclase and quartz as predominent minerals. Veins of Pegmatites and Quartz often appear interspersed with these rocks. Spheroidal weathering, occassional joints and irregular fractures are common in these rocks.

2. Granitoid gneisses and garnetiferous biotite gneisses :

Granitoid gneisses including garnetiferous biotite gneisses and granite gneisses ocupy the bulk of basin area. The rocks are finely foliated and display bedded character often intruded by thin veins of pegmatites and quartz. The trend of foliation is NE, SW with 45^0 to 75^0 dip in SW and WNW direction. The texture is medium to coarse grained. The rocks are light coloured consisting of white felspars and quartz, pink garnets with flakes of mica.

3. Garnetiferous sillimanite gneisses :

Sillimanite bearing garnetiferous gneisses occur as two distinct bands in the south western part of the basin. The bands are well foliated and have a trend NW-SE and dip $30^0$to 50^0towards SW-direction.

4. Calc-gneiss, Calc-granulites and crystalline limestone:

These rocks are often massive, coarse grained and occur as thin linear bands traversing the gneisses. But finer and medium grained, impure micaceous varities are also common.

5. Quartzites:

These rocks occur as distinct and detached linear bands on

knife edge ridges within the gneisses and charnockites in the central plain of the basin area and form low hills, knolls and high grounds, often associated with calc-gneisses and granulites. The rocks are coarse textured, granular, white to light reddish in colour, with thin streaks of iron ores The trend of quartzites varies from NW-SE to NE-SW with very steep dips. It is claimed that the direction of flow of the Tambraparni river is controlled by these ridges.

6 Tertiary formations.

The tertiary formations of marine sandstone and shell limestones unconformebly overlie the crystalline rocks as patches. The rocks are fine to medium grained hard white sandstones, calcareous and shelly limestones and some times grade into arenaceous limestones.

7. Recent to subrecent formations:

(a) Laterite :

Red and reddish brown, porous varigated laterites occur admixed with grits and pebbly materials. A few occurrences are found along the quartzite hills in the north.

(b) Kankar :

Kankar outcrops are seen as patches along stream courses. This material is hard and compact, calcareous to siliceous and frequently contains quartz.

(c) Shell limestone:

The sandy coastal belt is underlined by loose textured, coarse caleareous grits, shell limestone and calc-sandstones for a width of 3 to 5 km.

(d) Alluvium :

Alluvium comprised of admixtures of medium to coarse grained sand, gravel and silt occur along the Tambraparni as narrow belt and also in the delta area. Dark coloured stiff plastic clays also occur at the base of the alluvium.

(e) Teri Sands (Red):

Thick accumulation of wind blown red sand dunes commonly known as "Teri Sands" cover a large portion of the coastal area. These sands are composed of red stained quartz grains with an admixture of fine red clayey dust and a small amount of ilmenite.

(f) Coastal Sands(White) :

A narrow strip of wind blown coastal sands occurs, parallel to the coast, comprising of medium grained white sands mixed with particles of recent shells and garnet.

(g) Soils :

Black cotton soils are observed in the northern and north eastern portion of the basin area. The black soil is fine clayey earth, porous and has a thickness of 0.5 to 5 m. Red soils occur as thin capping over quartzites and garnetiferous gneiss.

2.2 Water quality :

Only a few published papers are available on ground water and river water quality in the Tambraparni Basin. Balasubramanian et al (1985) evaluated electrical conductivity and concentration of Cl and Na+K in ground water. They prepared contour maps showing the variation of these parameters. They also made an attempt to delineate the fresh water and salt-water interface and to demarcate the potable ground water potential zones using geophysical and geochemical investigations. According to them .

ground water occurs under both water table and confined conditions in this basin. The shallow water table is encountered towards the coast and the deep water table to the western regions of the coast in the basin. They conculded that the occurrence of thick permeable sandy layer along the coastline make the salt water intrude in to the coastal aquifers.In additıon ,ground water in the black cotton soil area also have saline water conditions.

Institute of water studies, Madras (1986) calculated the total water potential available in Tambraparni basin to be 1176 mm^3. The annual total requirement for all industries is 54.175 mm^3 (4.64% only).

Balasubramanian and Sastri (1987) extended the previous Balasubramanian et al (1985) work on quality of ground water of Tambraparni River basin. They prepared maps to project the regional quality behaviour of ground water on the basis of (1) TDS (2) Hardness (3) Salinity and Sodium hazard (4) Index of Base exchange (5) cation-anion types and (6) Corrosivity. They demarcated the aquifers according to various uses like household, drinking, irrigation and industry. They also studied the mechanisms responsible for the controls of ground water chemistry.

Haniffa et.al (1993) analyzed physico-chemical and microbiological parameters in selected water samples from the river Tambraparni. They observed that a continuous discharge of sewage and effect from domestic and industrial source finds its way into the river, and these pollutants influence the river water quality and biological parameters. They concluded that the

biological activity was high in the lower reaches of the river by calculating the index of faceal coliform contamination.

2.3 Behaviour of dissolves silica and phosphate in estuary

It has been clearly established that estuaries play an important role in controlling river input to oceans. The mixing of fresh water (river) and salt water (sea) end members starts off a variety of physico-chemical reactions. Special attention has been given to the elements, Si and P because both are biogeochemically active and behave in a non-conservative manner. This means that the variation of their concentrations from river mouth to open sea does not fall along the theoretical dilution line. These line is generated by joining the points for the end members in a plot against chlorinity or salinity values.

2.3.1 Silica

The concentration of soluble silica in river water is ten to fifteen times that of surface-water in the open ocean. In spite of the large amount of soluble silica that is brought into the ocean, there is no sight of an accumulation of souble silica in surface sea-water. Bien et. al (1958) tried to interprete the removal of dissolved silica in the Mississippi estuary. They proposed two hypotheses to account for the depletion of soluble silica (1) biological removal during periods to high discharge and (2) inorganic precipitation. They also proposed two mechanisms of inorganic precipitation (1) reaction of soluble silica with electrolytes in seawater resulting in salt formation and (2) adsorption or co-precipitation of soluble silica with suspended solids or collidal material in river water as these come in contact with electrolytes.

Davis (1964) had observed that silica in river water did not show dilution effect upto the expected level during storm run off. He concluded that this was because the high concentration of suspended particles release silica at a rapid rate.

Wollast and De Broeu (1970) concluded that in the estuary of the Scheldt river the removal of silica from the solution is not due to a reaction with clay minerals in suspension but to bilogical activity, essentially diatoms that live preferentially in saline water.

Purushothaman and Venugopalan (1972) investigated the distribution of dissolved silicon in the Vellar estuary of Tamil Nadu. They observed the highest value of dissolved silicon at the upstream part and a close negative correlation between silicon and salinity towards the sea. They observed different amounts of deviation from linearity during different seasons.

Ray et.al (1984) found that in the Mahanadi esuary silica concentration was depleted with respect to the theoretical dilution line particularly during non-monsoon periods and the removal appeared to be biological since the particulates revealed several siliceous micro organisms like diatoms under a Scanning Electron Microscope. During monsoon periods there appear to be no silica removal in the estuary which was discharging fresh water even at the river mouth.

Ramanathan et. al. (1993) concluded that in the Cauvery estuary silica is controlled by (1) natural river input, (2) adsorption by clay minerals and (3) physical mixing. These authors observed a rapid removal of silica in the estuary but

felt that no biological process has yet been identified to account for the depletion of silica.

2.3.2 Phosphate

Dissolved phosphate is a minor constituents of river and sea water but is of considerable environmental significance because of its role in supporting the growth of algae and various micro organisms. The most interesting aspect of phosphate in estuaries is its complicated adsorption and desorption behaviour with respect to the suspended load of river. Berner and Berner (1987) give a detailed description of dissolved phosphate in estuaries. Some critical data are reviewed below.

One of the earliest work on this topic was carried out by Upchurch et.al (1974) in the Pamlico estuary of U.S.A. They recorded an initial adsorption of phosphate by sediments and later desorption in the higher salinity zone. Similar results have been reported by Maest et. al (1990) in USA and Ramanathan et. al (1988, 1993) in the Cauvery estuary. Most authors including Fox (1990) and Berner and Rao (1993) believe that iron oxides present in the river sediments strongly influence the adsorption of phosphate. This was confirmed by the experimental work of Raymahashay et. al (1990) where lateritic soil showed greater adsorption and retention of phosphate compared with Black Cotton soil. Both soils were less effective for phosphate removal from saline solutions. The overall conclusion is that the decrease in phosphate adsorption in salt solution is possibly the outcome of three processes : (1) lower anion uptake at higher pH, (2) flocculation of surface active clay colloids and (3) competition between chloride and phosphate anion.

Subramanian (1993) concluded that Si and P shown opposing behaviour in the sense that Si shows drastic decrease where as P has an increasing trend in the higher salinity part of the Ganges estuary. In the latest study of the Cauvery estuary Ramanathan et.al (1993) also report a general increase of phosphate in down stream with irregular variation. They also point out the possible derivation of phosphate from phosphatic nodules in sedimentary rock in the drainage basin, contribution of phosphate due to intensive use of fertilizers and removal by adsorption on to sediments in the estuary zone.

2.4 Mechanism of Adsorption-Desorption by River Sediments

2.4.1 Ion Exchange properties of clay

We know that the clay minerals have the property of exchanging anions and cations with water at the clay-liquid interface. More information is available regarding exchange of cations primarily because clay particles are negatively charged in aqueous suspension. In precise work, cation exchange capacity (CEC) is expressed as milliequivalent per 100 grams at pH 7. The main factors leading to CEC are (1) unsatisfied charges produced by broken bonds at surface and edges of the particles (2) unbalanced charges caused by isomorphous substitution of cations (3) lattice defects (Carroll, 1957). Among the clay minerals commonly present in soils and sediments, montmorillonite shows highest CEC value of 80-150 me/100 g and kaolinite the lowest value of 3-15 me/100g. This difference is due to the nature of exchange sites in the clay lattice. The CEC of illite is in between the values of kaolinite and montmorillonite.

Although, theoretically, the anion exchange capacity (AEC) can be treated in a manner similar to CEC, interpretation of anion uptake is much more difficult because of the possibility of decomposition of clay structure. Most theories about anion exchange have been associated with adsorption of phosphate (Phosphate fixation) by soils. According to Grim (1968) there has been a considerable argument as to whether adsorption of phosphate by kaolinite involves (1) replacement of OH ions by phosphate ions (2) a reaction between phosphate and alumina produced by the distribution of kaolinite lattice. Another mechanism proposed is similarity of size and geometry of SiO_4 tetrahedran and the po_4^{-3} molecule. More recently, Stumm and Morgan (1970) and Morel (1973) have proposed ionization of the functional groups at the clay surface for anion uptake. Therefore, AEC is more prominent at low PH and CEC increases with increasing pH. Grim (1968) reports the average ratio of CEC to AEC as 0.5 for kaolinite 2-3 for illite and 6.7 for montmorillonite. The exchangable ions retained by clay minerals are subjected to two types of attractive forces (1) weak Vander Waals force where the ions are easily desorbed (2) stronger attractive force causing chemisorption of ion on the clay mineral structure.

2.4.2 Clay colloid

The atomic structure of clay minerals and ion exchange properties are inter related through the behaviour of clay suspension as a Sol or colloidal suspension. Majority of the clay flakes have thickness in the colloidal range (10^{-3} to 10^{-6} mm i.e. 1 μm to 1 nm) whereas the particle may exceed the upper limit of colloidal size. Some important properties like surface

charge, exchange and adsorption of ions from solution, Brownian movement, Flocculation by electrolytes are all typical of colloid behaviour (Krauskopf, 1979).

A net negative charge on clay colloids can be demonstrated by migration of particles towards a positive electrode during electrphoresis. On the other hand, there is considerable evidence to support that two types of charges exist on a clay particle. The flat surfaces have a negative charge whereas the particle edges have both positive and negative sites (Wayman 1967). As the area of the flat surface is much larger than the edges, the net charge on the particle is negative.

The main reason for a deficiency of positive charge on the flat surface is isomorphous replacement of Si^{+4} by Al^{+3} in the T-layer or Al^{+3} by Mg^{+2} in the O-layer. On the other hand, at the edge of the particle, T and O layer are disrupted. Broken bonds like Si-O-Si or Al-O-Al create a positive charge where as Si-O-Si-O or Al-O-Al-O would give rise to negatively charge sites.

In a clay sol, the particles charges are internally compensated by the development of an electric double layer (Van Olphen 1977). This double layer consists of the charged particle surface surrounded by a diffuse layer of counter ions of opposite charge. Thus the flat surface will have a double layer with the diffuse layer of positive ions whereas the particle edges may have a double layer with the diffuse layer of negative ions. The concentration of counter ions gradually decreases away from the clay-water interface.

In a salt free suspension of clay in water, there are two

types of forces acting on the surface (1) repulsive forces between similar charged partides (2) attractive forces (Vander Waals) between the particles. When an electrolyte is added, oppositely charged ions from the solution, compress the double layer and attractive forces slowly overcome the repulsive froces. Therefore when two particles collide, they stick to each other and create a larger sized particle or 'floc'.

2.4.3 Role of Iron Oxide

The structure of iron oxide in aqueous solution gets charged due to adsorption of either H^+ or OH^- ions from the solutions. (Schwertmann and Taylor, 1977). So the charge of the iron oxide with depend upon pH of the solution.

An excess of positive or negative charge at the surface is balanced by an equivalent amounts of anions (A^-) or cation (C^+) either by nonspecific adsorption or by specific adsorption or both. The role of iron oxide on adsorption was further explained by Raymahashay et.al (1990) who found out that lateritic soils which contained a mixture of clay minerals and iron oxide were the most efficient for phosphate fixation.

Role of Organic Matter

It is highly probable that soil organics ;play an important role in holding phosphate through complex formation. Sholkovitz (1976) concluded that dissolved organic matter in river and estuary water controls the non-conservative behaviour of inorganic constituents like Fe, Mn, Al and P.

2.4.4 Dissolved Phosphate Species

Phosphorous is transported by river water in two principal forms, (1) dissolved (2) adsorbed. Out of a total of $2x10^{12}$ grams per year of dissolved phosphate transported in river run off, about half is present as inorganic phosphate, which is mostly orthophosphate ions (H_3PO_4, $H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3}). The rest is believed to be dissolved organic phosphorous (Berner and Berner, 1987).

The distribution of the orthophosphate anions are pH dependent as shown by the following equilibrium constant values (Krauskopf, 1979).

$$PO_4^{-3}+H^+=HPO_4^{-2}$$

$$K_1=\frac{a\ H\ PO_4^{-2}}{a\ PO_4^{-3}\quad aH^+}=10^{12.4}$$

Hence, $aHPO_4^{-2} = a\ PO_4^{-3}$ at pH = 12.4

Similarly, $HPO_4^{-2} + H^+ = H_2PO_4^-$

$$K_2=\frac{a\ H_2PO_4^-}{aH\ PO_4^{-2}\quad aH^+}=10^{7\ 2}$$

$$aH_2PO_4^- = aHPO_4^{-2} \text{ at } pH = 7.2$$

Also, $H_2PO_4^- + H^+ = H_3\ PO_4$

$$K_3=\frac{a\ H_3PO_4}{aH_2PO_4^-\ .\ aH^+}=10^{2\ 1}$$

$$aH_3PO_4 = aH_2PO_4^- \text{ at } pH = 2.1$$

At river and sea water pH values(7 to 8) the main species are HPO_4^{-2} and $H_2PO_4^-$. These anionic orthophosphate species are adsorbed on river sediments because of positively

charged sites on clays, iron oxide colloids and possibily on organic matter.

2.4.5 Dissolved silica species:

SiO_2 dissolves in water according to the reaction $SiO_2 + H_2O = H_4SiO_4$. Here, H_4SiO_4 or $SiO_2 . 2H_2O$ or $Si(OH)_4$ represents the neutral dissolved silica species which is most common in the pH range of river or sea water. This is because it dissociates to a negatively charged species according to

$$H_4SiO_4 = H_3SiO_4^- + H^+$$

The equlibrium constant

$$K_1 = \frac{a\ H_3SiO_4^- + H^+}{H_4SiO_4}$$

has avalue around $10^{-9\ 9}$ at room temperature (Stumm and Morgan, 1970). Therefore, $H_3SiO_4^-$ concentration exceeds H_4SiO_4 concentration only above pH=9.9. Above this pH value solubility of SiO_2 increases with pH according to the relation.

$$\text{Log } a\ H_3SiO_4^- = pH + \text{Log}k_2 \quad \text{where}$$

k_2 is the equilibrium constant of the reaction

$$SiO_2 + 2H_2O = 2\ H_3SiO_4^- + H^+$$

$$k_2 = aH_3SiO_4^- . aH^+$$

The value of k_1 (and k_2) depends on the SiO_2 solid phase undergoing solubility. It is known that the solubility of quartz is around 6ppm SiO_2 and that of amorphous silica is around 120 ppm SiO_2. Other solid phases have solubility in between these two values.

CHAPTER 3

METHOD OF WORK

The work for this thesis consisted of geological observation and sample collection in the field as well as analysis of sediment and water samples in the laboratory.

3.1 Field Work

The first field trip was undertaken in June, 1994, i.e., in the pre-monsoon period. After observing the landscape and the nature of the Tambraparni estuary, 3 sample sites were selected in the river water zone in the upstream part and 3 more in the downstream part of the estuary where sea waves were found to advance into the river. The sites are shown on Fig. 3.1.

The interval between sites 1, 2 and 3 in the river water zone is approximately 500 m. The distance between site 3 and site 4 (located in the beginning of sea water mixing zone) is approximately 4 km. The next sites 5 and 6 are 300 m and 500 m from site 4. The last site (6) is practically in the open sea.

Water samples were collected in polythene bottles from near the bank in the river water zone. To reach the shallow middle part of the estuary, a boat was used to cross the lagoon from the shore. Water samples were collected as before. At the same site where water was collected, the bed material from the bottom of the shallow water was scooped out for mineralogical study.

During microscopic and X-ray diffraction study of the bed material collected during the first trip, it was observed that the samples were largely sandy with very little clay. Therefore, another field trip was taken in June 1995 (under similar climatic condition as the first trip) to collect finer sediments from the

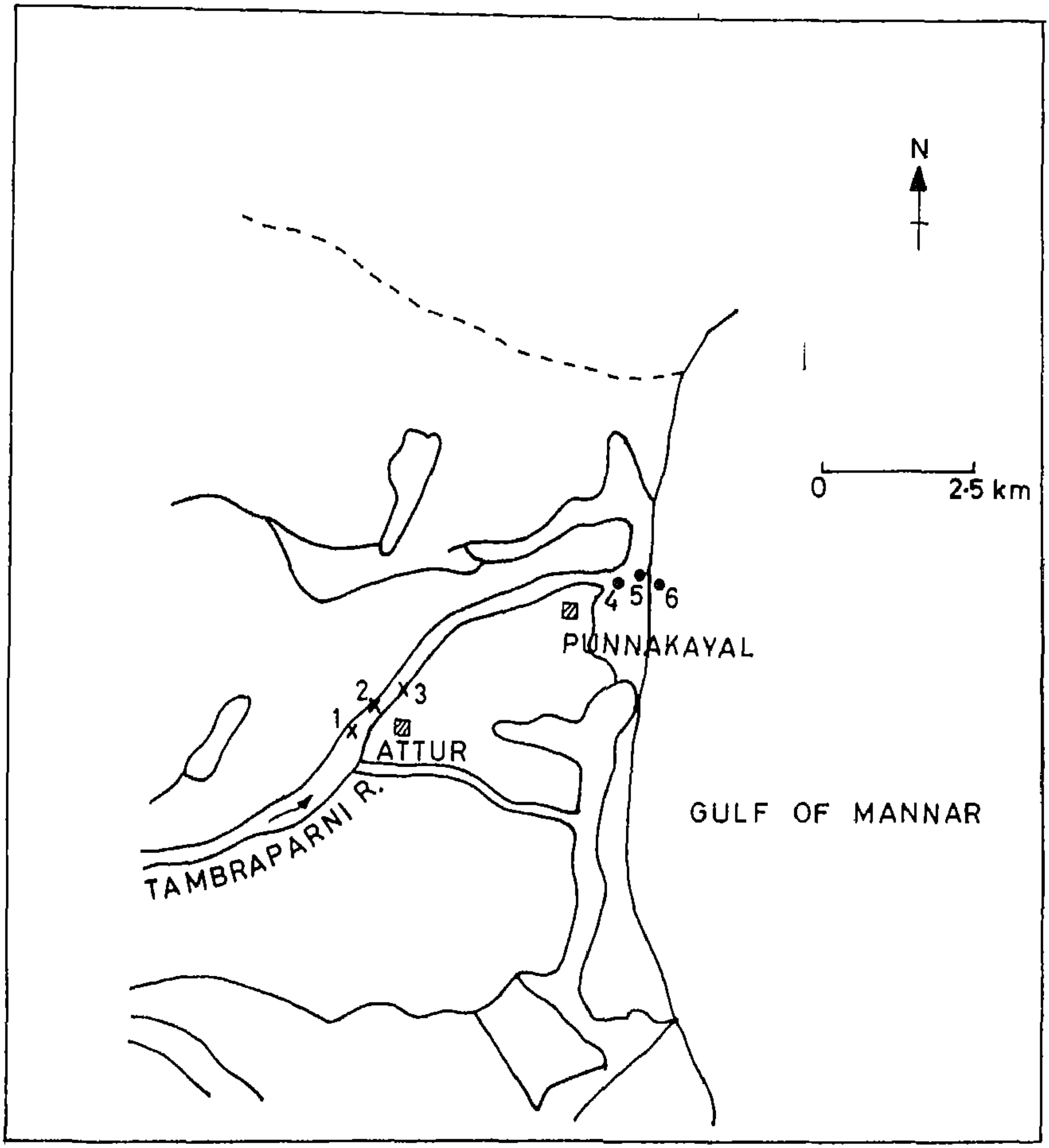


Fig.3.1: Location of sampling sites

river bank and flood plain which is roughly 200 m wide during this period. The field map was finalized during this trip by filling the gaps on landforms and landuse.

3.2 Laboratory Work

The water samples were analysed for pH, conductivity, TDS, Chloride, phosphate and silica. In addition, phosphate in sediment was determined by leaching in an acid mixture. A brief outline of analytical procedures (Standard Methods, 1965) is given below.

The sediment samples were observed under a binocular microscope. For the finer fraction (-200+240 sieve), X-ray diffractograms were obtained from bulk powder and oriented specimens prepared by drying a suspension on a glass slide.

3.2.1 Apparatus Used:

The following apparatus were used to carry out the experiments :

1. Systronics type 335 digital pH meter (Systronics, Naroda)
2. Systronics type 304 D.D.R. Conductivity Meter (Systronics, Naroda)
3. Systronics 103 Spectro Colorimeter (Systronics, Naroda).
4. DEBYEFLEX 2002 (Automatic Powder X-ray Diffractometer, Scietert and Co., U.S.A.)
5. Hot Air Oven (Adair Dutt and Co., Calcutta)
6. K-12 (Super) Analytical Single Pan Balance (K. Roy and Co., Varanasi)
7. Binocular Microscope (Bausch and Lomb, U.S.A.)
8. Type 21H, Magnetic Stirrer (Remi Corporation)
9. Standard Sieves and Laboratory Glassware

3.2.2 Conductivity and TDS

Conductivity is a numerical expression of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions, their total concentration, and on the temperature of measurements. Solutions of most inorganic acids, bases and salts are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct current very poorly. From this conductivity measurement, we can estimate total dissolved solids in a sample by an empirical factor. This factor may vary from 0.5 to 1.0, depending on the soluble components of water and temperature of the measurement. For the fresh water samples (1, 2 and 3) TDS values were calculated by multiplying the measured specific conductivity in umhos/cm at 25°C by a factor 0.65. The conductivity meter was calibrated with standard KCl solution. The TDS values for the three saline water samples (4, 5 and 6) were determined by evaporation method. For this 50 ml of the samples was completely evaporated in a pre-weighed beaker and the amount of salt deposited was calculated by weight difference. The TDS was expressed as mg/l from the above measurement.

3.2.3 Chloride

Chloride, in the form of Cl^- ion, is one of the major inorganic anions in water. In water the salty taste produced by chloride concentrations is variable and depends on the chemical composition of water. Some waters containing 250 mg Cl^-/l may have a detectable salty taste if the cation is sodium. Here we have used the Argentometric method to calculate the chloride content of the water samples.

In a natural or slightly alkaline solution potassium chromate can indicate the end point of silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed. Potassium chromate indicator solution was prepared by dissolving 50g of potassium chromate in one litre distilled water. Standard siver nitrate solution of strength 0.0141N was prepared by dissolving 2.395 g $AgNO_3$ in distilled water and diluting to 1000 ml. 100 ml of five times diluted fresh water samples and 100 ml of 1000 times diluted saline water samples were used in this titration. The samples were titrated with standard $AgNO_3$ after adding 1.0 ml K_2CrO_4 indicator solution. The end point was observed as pinkish yellow colour. This titration was also done for blank (distilled water used for dilution). Chloride was estimated from the following formula.

$$\text{mg } Cl^-/l = \frac{(A-B) \times N \times 35450}{\text{ml sample}}$$

Where,

A = ml titration for sample

B = ml titration for blank

N = Normality of $AgNO_3$ which is equal to 0.0141

3.2.4 pH

pH was measured after calibrating the pH meter with a pH 7 buffer at the temperature of the sample. The result was obtained as a digital output.

3.2.5 Phosphate

Total orthophosphate in water samples was determined by the calorimetric stannous chloride method using an acid ammonium molybdate reagent. The basic principle is to form an ammonium

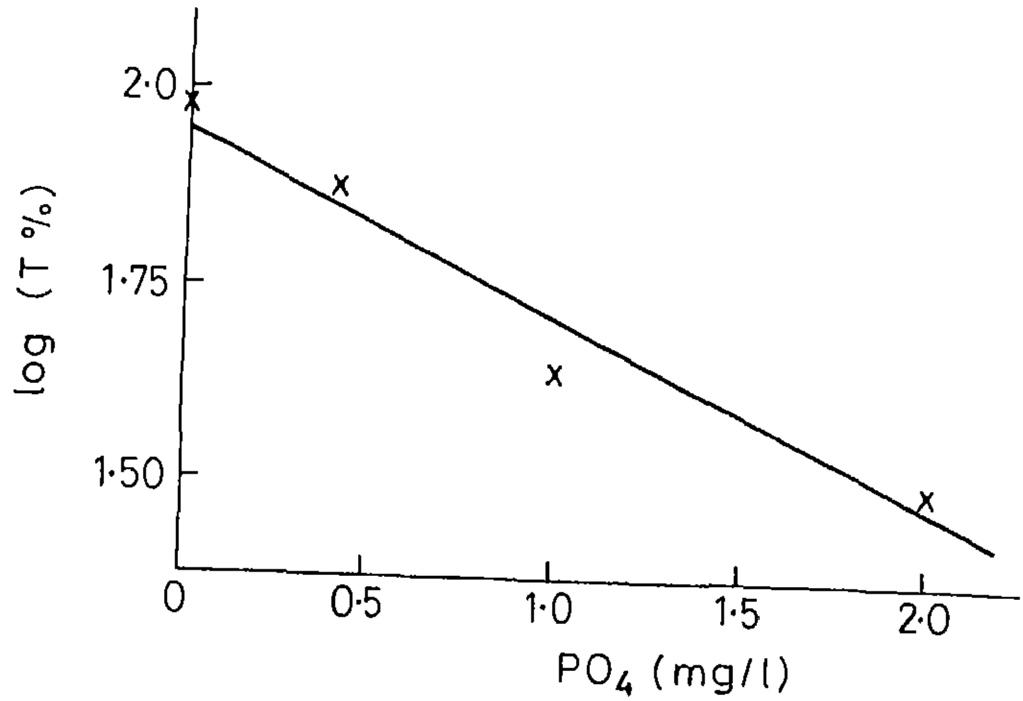


Fig.3.2: Calibration curve for phosphate

phospho-molybdate complex which is reduced by $SnCl_2$ to give a blue coloured solution. The intensity of blue colour is proportional to phosphate concentration. Calibration curves were prepared by using phosphate standards and transmission was measured at 690 nm in a spectro colorimeter. A linear relationship was obtained between log T and mg/l phosphate. A typical calibration curve is shown in Fig. 3.2. The accuracy of this method is of the order of 2 percent.

3.2.6 Silica

Total dissolved silica in water samples was determined by the colorimetric molybdosilicate method. The principle is that ammonium molybdate at pH approximately 1.2 reacts with silica and any phosphate present to produce heteropoly acids. Oxalic acid is added to destroy the molybdophosphoric acid but not the molybdosilicic acid. The intensity of the yellow colour is proportional to concentration of 'molybdate - reactive' silica. Calibration curves were prepared by using silicate standards and transmission was measured at 470 nm in a spectro calorimeter. A linear relationship was obtained between log T and mg/l silica. A typical calibration curve is shown in Fig. 3.3.

3.2.7 Extraction of Phosphate from Sediments

Various methods for extracting P (Phosphorus) from soil and sediments are available in literature. For example, Jackson (1962) recommends determination of acid soluble P by extracting soils by 0.002 N H_2SO_4. On the other hand, Black (1965) comments that mixed acid is better for extraction of P in soils. He recommends the mixture of 0.05N HCl and 0.025 N H_2SO_4 for this

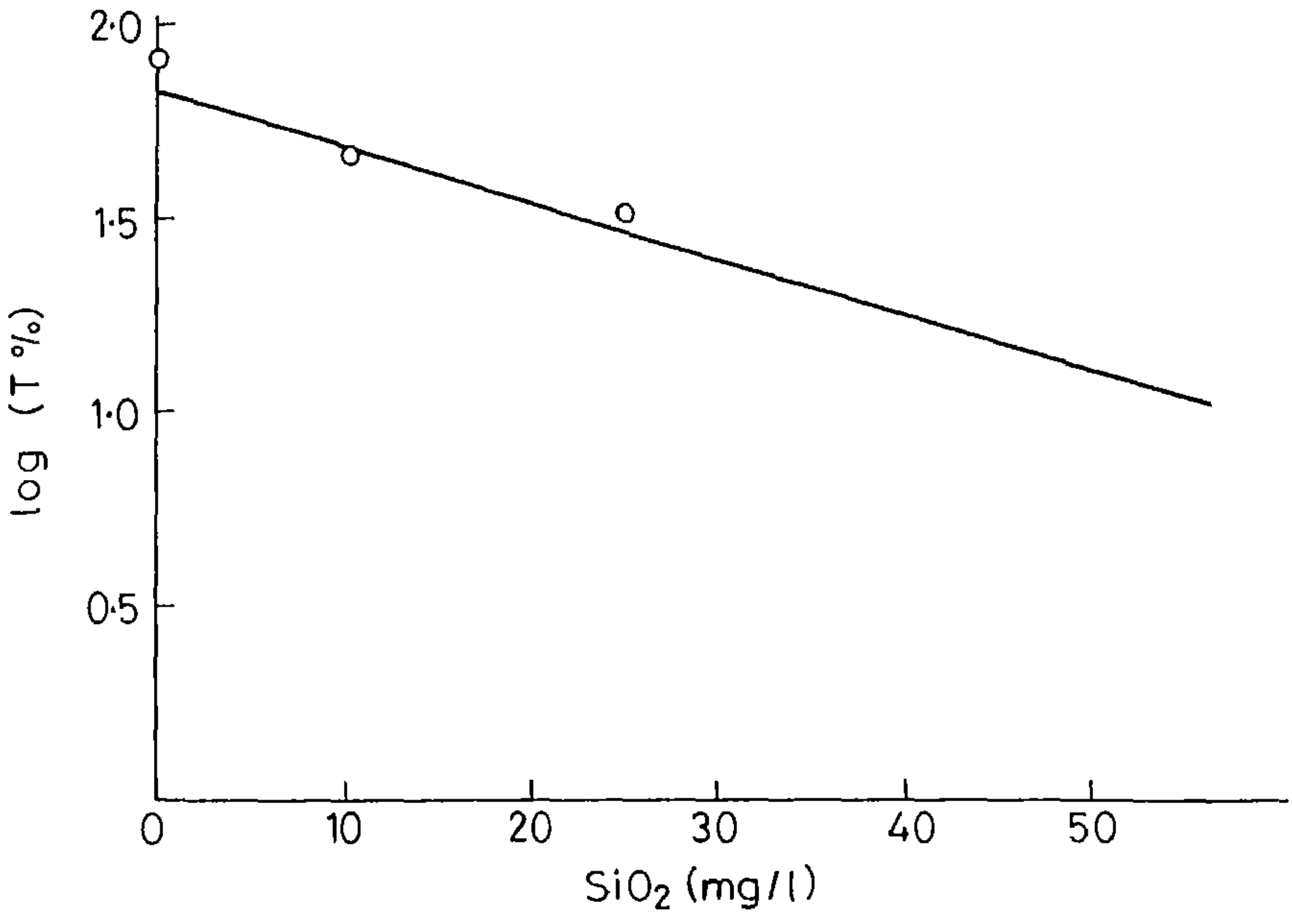


Fig.3 3: Calibration curve for silica

inorganic P in estuary sediments was determined by extraction in 1 N HCl at room temperature. Taking these methods into consideration, an extracting solution was prepared by the following method.

15 ml of approximately 1 N HCl (0.0998 N by NaOH titration) was diluted to 300 ml. 215 ml of this dilute HCl was mixed with 0.03 N H_2SO_4 (strength determined by NaOH titration) to give a final volume of 250 ml. This final solution contained 0.04 N HCl and 0.004 N H_2SO_4 which was used for phosphorous extraction as described below.

10 g of sieved (-200, + 240 size) sediment sample was mixed with 40 ml of acid leachate mentioned above. After continuous stirring for 10 minutes in a magnetic stirrer, this solution was filtered through Whatman 42 filter paper. From this 25 ml of the solution was taken for phosphate analysis by the colorimetric method described for water samples.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Sampling Sites

Since this study is mainly concerned with geochemistry of sediment and water in the estuary area of Tambraparni river basin, the sample sites were selected in the coastal area of this basin. Physiographically, the total basin area can be broadly divided into three units (Inst. of Water Studies, 1986), namely ,

1. Western mountainous terrain with valley complexes.
2. Central elevated terrain
3. Eastern coastal plains

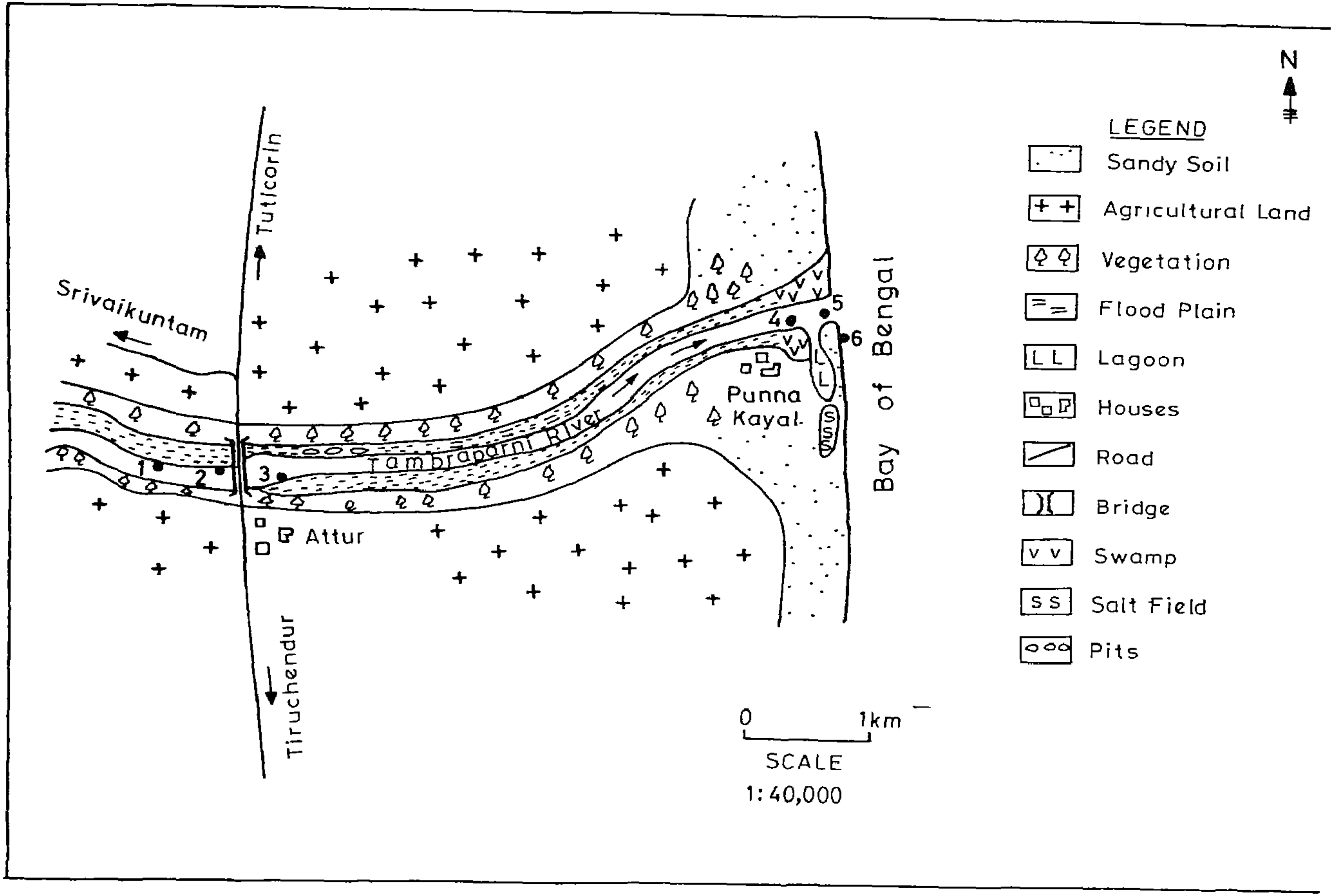
All the sampling sites are located in the third unit (Eastern Coastal Plains).

The three fresh water sample sites were selected near the village Attur which is around 26 km away from Tuticorin in Southward direction, where the Tambraparni river flow in a W-E direction. Here the river water is potable. It is used for agricultural and domestic purposes.The width of the entire river valley is around 400 m (Fig. 4.1) of which the width of flood plain is around 200 m. The three saline water samples were collected near the village Punnakayal, which is around 5 km away from Attur in eastward direction, where the Tambraparni river is mixing with the sea. Fig. 4.1 is a sketch map prepared in the field which supplies the following geological information.

4.1.1 Geology

The study area mainly consists of recent deposits in the form of alluvium, Teri sands(aeolian sands), coastal alluvium and soils.

Fig.4.1: Map showing local geology and land forms



(a). Alluvium

Alluvium is comprised of admixture of medium to coarse grained sand, gravel and silt occurring along the flood plains of Tambraparni river as a narrow belt and also in the delta area. Previous work (Inst. of Water Studies, 1986) has indicated that sand stones and shell limestones underly the alluvium.

(b) Teri Sands

Thick accumulation of wind blown red coloured sands locally known as 'Teri sands' was observed near Attur village. The Teri sands are composed of red stained quartz grains with an admixture of fine red clayey dust.

(c) Aeolian Sands(White)

A narrow strip of wind blown coastal sands occurs, parallel to the coast, comprising of medium grained white sands mixed with particles of shells and garnet. This was observed near the village Punnakayal.

(d) Soils

Alluvium and aeolian soil occur in the Tambraparni delta area between Attur and Punnakkuyal villages. These soils mainly contain sand and silt materials.

4.1.2 Geomorphology

The main land forms observed in the field are mostly fluvial land forms, coastal land forms and aeolian Land form.

(a) Fluvial Landforms

A narrow, band of flood plain has developed on either side of Tambraparni river near Attur village. It widens as a broad alluvial plain towards the coast near Punnakayal village. Medium to fine grained sand, silt, and lenses of clay are present in

these flood plain. These are bordered by terraces at a slightly higher elevation which are covered by vegetation and agricultura land.

(b) Aeolian Landforms

Wind action has developed active sand dunes/ridges parallel to the coast. These sand dunes were observed on the coast near Punnakayal village and Tiruchendur. The sand dunes are comprised of white sand and silt material.

(c) Coastal Landforms

Coastal landforms such as beach sand dunes, beach terrace, beach ridges were observed in the Punnakayal and Tirchendur area. These landforms are comprised of marine sediments such as silt,coastal sand,and recent shell frgments.The other coastal landforms like tidal fats,lagoons have also developed near Punnakayal village .

4.1.3 Land use

The various landuse categories of the study area is grouped into -

1. Agricultural land
2. Salt pans
3. Waste land
4. Water bodies

(1) Agricultural Land

The study area comprised of around 70% agricultural land. Intensively irrigated crop lands are developed on either side of river near Attur village. The major crops are paddy, sugar cane, ground nut, coconuts, plantain.

(2) **Salt Pan**

Most of the land near the coast from Tuticorin to Attur is used as salt pan. Tuticorin is one of the biggest salt production centers in the state of Tamil Nadu. Most of the land near Punnakayal village is used as salt fields.

(3) **Waste Lands**

Barren areas, sand dunes, grass lands, uncultivable waste,marshes and swamps are included in this category.Most of the land near Punnakayal village is waste land. Marshes and swamps have also developed near this village .

(4) **Water Bodies**

Large irrigation tanks and canals were observed near the village Attur, and some water logged areas were observed near the village Punnakayal.

4.2 Description of Sediments

4.2.1 Sieve Analysis

The bed material collected at station No. 1 after oven drying was subjected to sieve analysis. The results obtained from a total weight of 74 gm are given in Table 4.1

Table 4.1 Sieve Analysis

Sieve number	Opening (mm)	Weight retained (gm)	% of total weight
10	2.0	1.657	2.23
20	0.840	13.338	18.02
40	0.420	24.820	33.54
60	0.250	18.4	24.86
100	0.149	7.005	9.46
200	0.074	7.445	10.06

From the above data the sediment was classified into the following fractions as per standard nomenclature (Schultz and Cleaves, 1955) :

1. Coarse sand (+10 sieve) = 2.23%
2. Medium sand (-10, +40 sieve) = 51.56%
3. Fine sand (-40, + 200 sieve) = 44.38%
4. Silt and clay (-200 sieve) = 1.82%

It is clear from this analysis that the bed material carried by the Tambraparni river predominantly contains medium to fine sand size particles with negligible amount of silt and clay.

4.2.2 Description Under Binocular Microscope

Small quantities of the bed load material were observed under binocular microscope in order to identify the minerals present according to their physical properties. For example quartz was identified from subrounded crystals showing a variety of colour and conchoidal fracture. Transparent white varieties as well as red jasper were very common. The quartz grains frequently had a red coloured coating most likely by iron oxide. This contributes to the overall red colour of the sediments which finally is responsible for the name Tambraparni river. In a similar way felspar was identified from flat grains with cleavage; pyroxene from dark opaque grains with cleavage; garnet from deep red rounded grains; sillimanite from needle like aggregates brown and greyish in colour and muscovite mica from transparent cleavage flakes.

A summary of the minerals identified in the 6 samples collected along the Tambraparni river is given in Table 4.2.

Table 4.2 : Mineralogy of the Sediments under Microscope

Sample No.	Description
1.	Rich in red colour quartz. Lesser amounts of other varieties of quartz, felspar, pyroxene garnet, mica.
2.	Rich in quartz. Lesser felspar, pyroxene garnet.
3.	Rich in quartz and pyroxene.Lesser felspar, Garnet,mica,sillmanite,Shell frgments present.
4.	Rich in quartz. Lesser felspar, pyroxene, garnet, mica. More shell fragments than No. 3.
5.	Very rich in quartz, felspar and cryptocrystalline chalcedony. Lesser garnet, pyroxene, felspar, sillimanite. Shell fragments present.
6.	Rich in cryptocrystalline quartz (Chalcedony). Lesser pyroxene,felspar.Shell fragments present.

4.2.3 Interpretation of X-ray Diffractograms

A preliminary scanning showed that the X-ray diffractogram of all the six samples are dominated by quartz and felspar even in oriented slides. The river bed materials showed strong and sharp peaks of quartz (3.33, 4.21Å) A typical X-ray diffractogram of sample No. 3 from the fresh water zone is shown in Figure 4.2. It also contains sharp peaks of sillimanite (3.39, 3.45, 3.73Å). The X-ray diffractogram of sample No. 6 (Fig. 4.3) from the sea shore contains quartz, felspar and sillimanite peaks along with two peaks at 2.99, 2.48 Å which can be matched with pyroxene of augite variety. It is noted that the

X-ray diffractograms do not contain peaks of garnet which being a heavy mineral had apparently settled down during the preparation of a suspension for X-ray study.

As mentioned earlier, a special effort was made to collect clay samples from the river banks during the second field trip. Slides prepared from suspension of the finestfraction (-240 sieve) continued to show quartz and felspar peaks. However, there were broad and imperfect peaks of kaolinite and illite in these diffractograms A typical pattern is shown in Figure 4 4 for a bank sample collected at station 1 in the fresh water zone. A similar pattern was obtained at station 5 in the saline zone

The overall conclusion from X-ray studies is that the extent of chemical weathering is very limited in the catchment area of the Tambraparni river. As discussed earlier, the main rock types in the upstream part are granitoid gneisses dominated by quartz which is resistant to weathering The river is bringing unweathered fragments of quartz, felspar, sillimanite, pyroxene, and garnet to the mouth. This indicates that the rate of material transport is higher than the rate of chemical weathering and soil formation. This is a common situation in drainage basins with hard rocks and steep slopes as mentioned by Stallard (1984). The only evidence of limited chemical weathering is the occurrence of poorly crystalline kaolinite along with illite and gibbsite (?) in the bank sediments. It appears that while the coarse grained and rounded rock forming minerals are confined to the channel, colloidal and flaky clay minerals are deposited on the flood plains during periods high discharge when the river overflows the bank.

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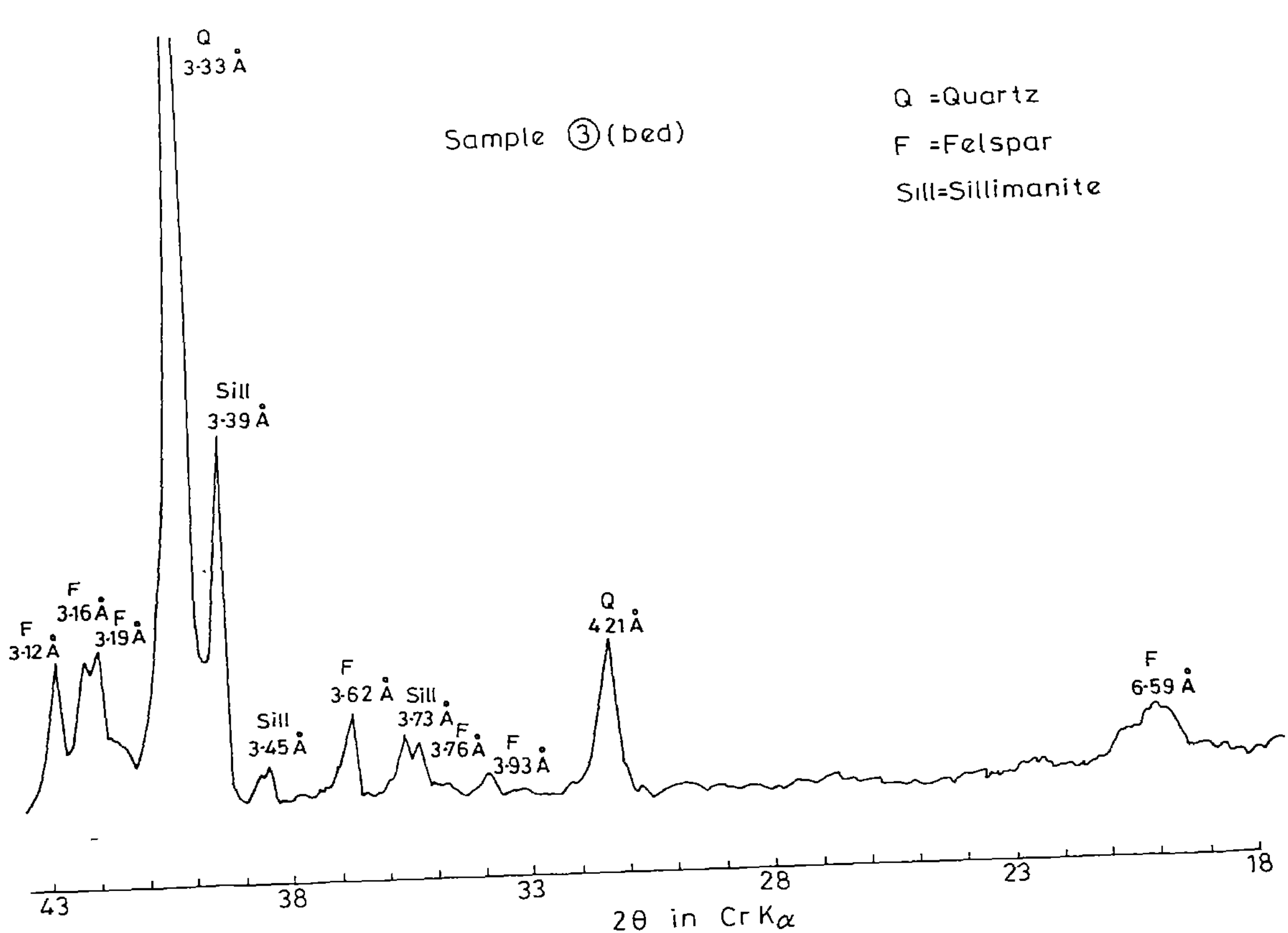


Fig.4.2: X-ray diffractogram of bed material at station.3

(Fresh water zone)

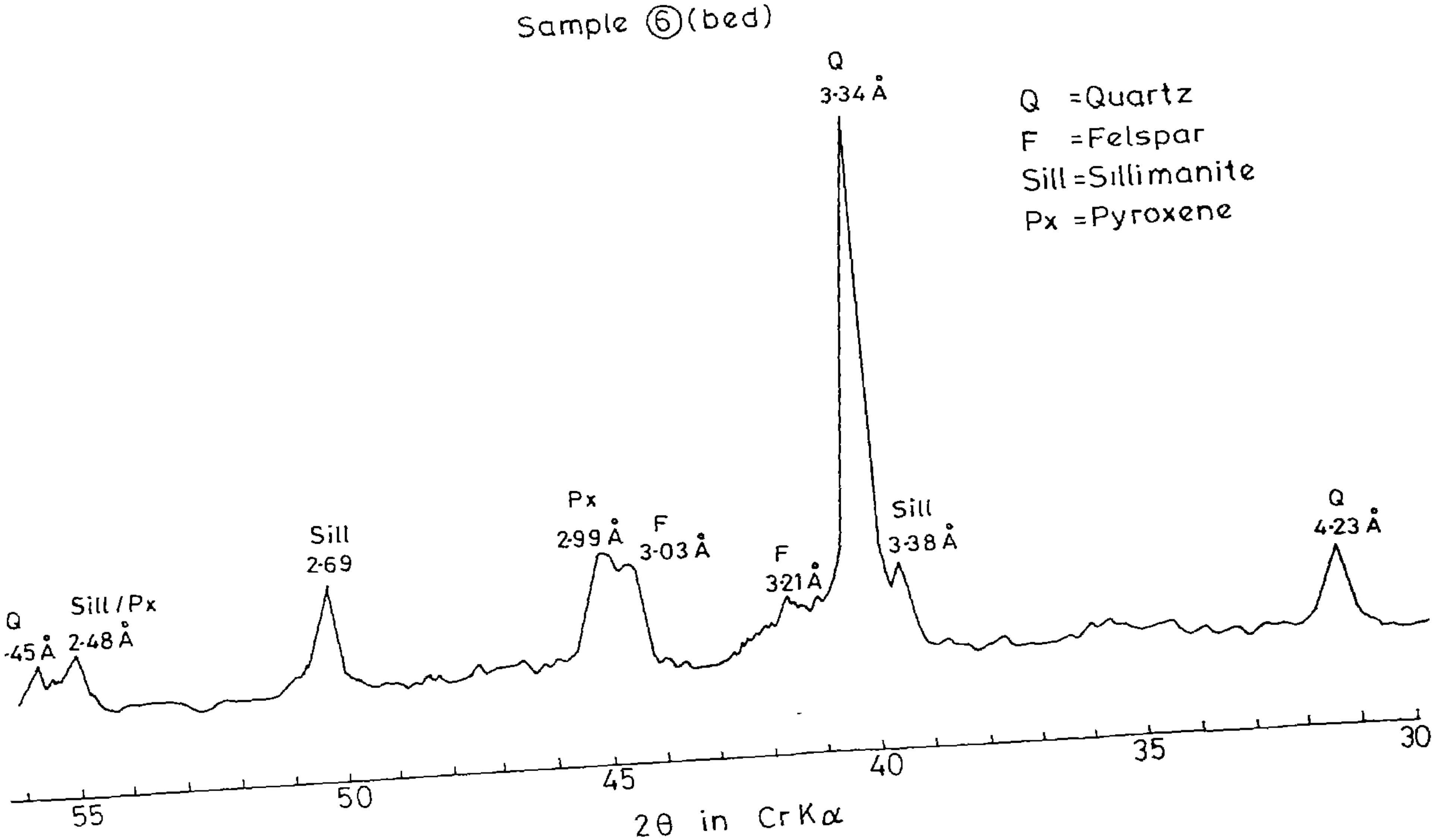


Fig.4.3: X-ray diffractogram of bed material at station.6

(Saline water zone)

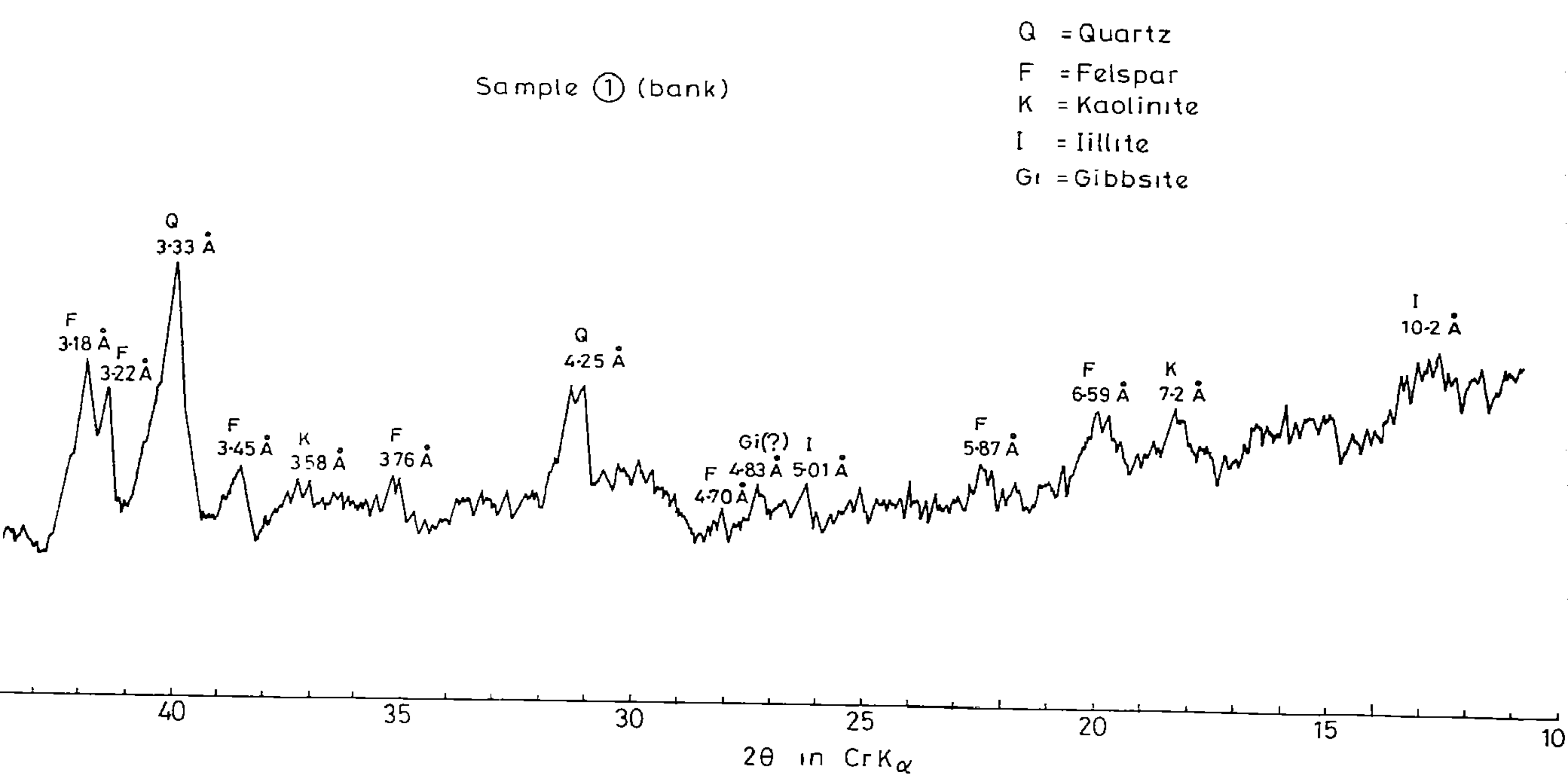


Fig.4.4: X-ray diffractogram of bank sediment at station.1

(Fresh water zone)

Although the sediments have reddish colour and iron oxide coated quartz grains are seen under the binocular microscope, no X-ray peaks of iron minerals were noticed. This indicates that the iron is in amorphous and colloidal phases.

4.3 Water Analysis

The main objective of this work was to compare the variation of dissolved silica and phosphate alongtheestuary.However,for acomplete picture,it was necessary to determine pH, TDS and Cl also.

4.3.1 pH

The pH values (Table 4.3) showed a general increasing trend towards the open sea. However, there were local fluctuations at station 3 and 4 which are at the mixing zone between fresh water and saline water.

Table 4.3 : pH values along Tambraparni estuary

Station No.	pH
1.	7.09
2.	7.31
3.	7.65
4.	7.11
5.	7.37
6.	7.60

4.3.2 TDS

Total dissolved solids (TDS) was determined by two methods. For the fresh water samples, where TDS was expected to be relatively low, an empirical relationship between specific

conductivity and TDS was utilized. Many authors (e.g. Hem, 1959) have found

TDS (mg/l) = A x Specific Conductivity (μ mhos/cm at 35°C)

where A ranges from 0.5 to 1.0 with an average around 0.65. The specific conductivity values determined for sample, 1, 2 and 3 and the calculated TDS values using A = 0.65 are given in Table 4.4.

Table 4.4 : Specific Conductivity and TDS in Fresh Water Samples

Sample No.	Specific Conductivity (μ mhos/cm)	Calculated TDS (mg/l)
1	660	429
2	750	487
3	880	572

It is noted that TDS progressively increases downstream in the fresh water zone. However, this method is not recommended for highly saline water because the discrepancy between conductivity controlled by ionic species and TDS increases considerably. Therefore, for the three samples from the saline zone (no 4, 5 and 6) TDS was determined by direct evaporation and weighing the salt residue as discussed in Chapter 3. The values given in Table 4.5 shows a several order of magnitude increase over the first three samples but the increasing trend towards the open sea is maintained.

Table 4.5 : TDS in Saline Water Samples

Sample No.	TDS (mg/L)
4	40,200
5	40,600
6	46,200

4.3.3 Chloride

Table 4.6 shows that Cl like TDS shows a considerable increase from the fresh water zone (Sample 1, 2, 3) to the Saline zone (sample 4,5,6) and an increasing trend is maintained towards the open sea. In both the fresh water and saline zones, Cl increases with increase in TDS (Fig. 4.5)

Table 4.6: Chloride and TDS relationship in Tambraparni Estuary

Sample No.		Cl (mg/l)	TDS (mg/l)
Fresh	1.	115	429
	2.	165	487
	3.	180	562
Saline	4.	24,492	40,200
	5.	27,991	40,600
	6.	29,491	46,200

4.3.4 Silica in Water

Table 4.7 lists the values of dissolved silica along with Cl and TDS values in the fresh water as well as in the saline water zone.

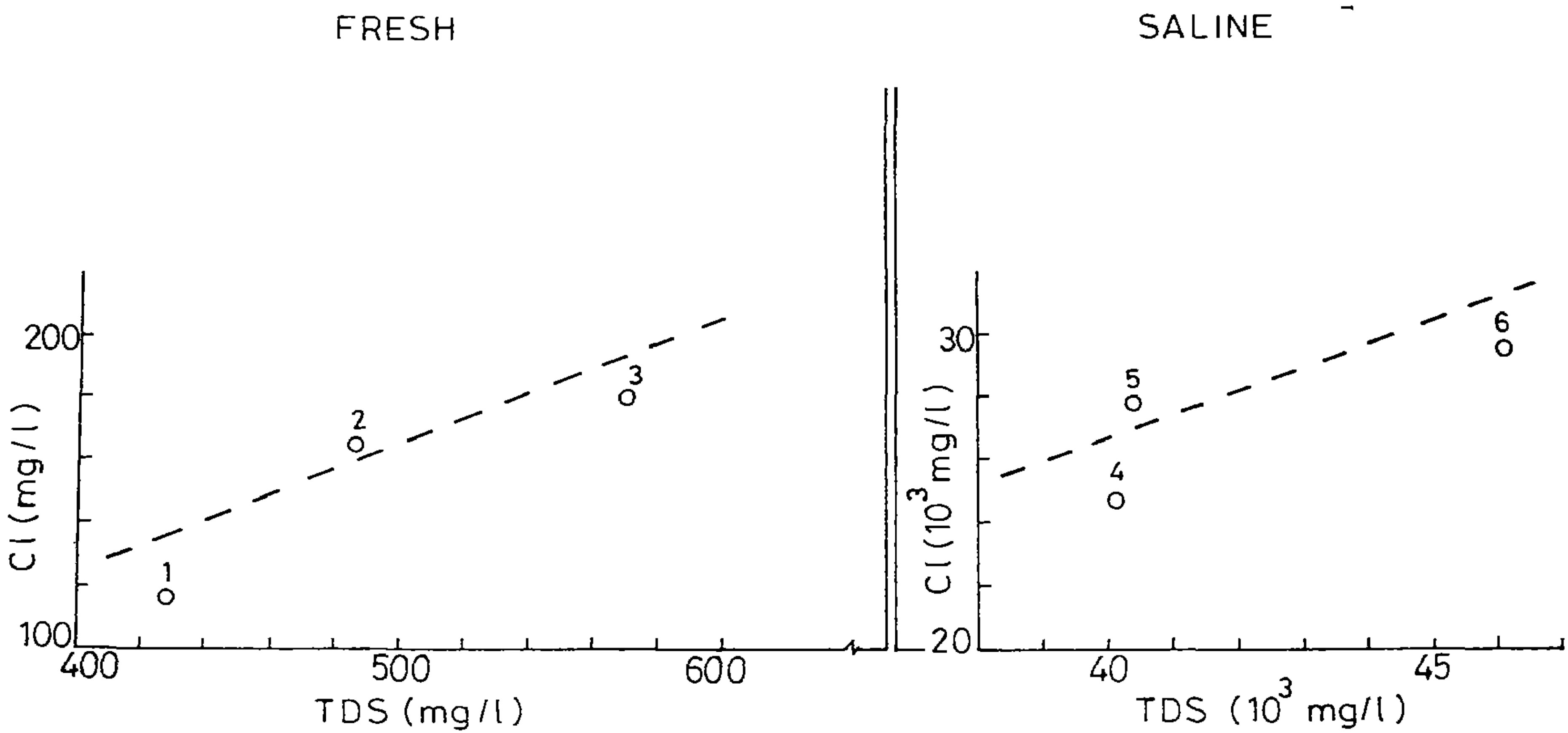


Fig.4 5: Variation of TDS and Chloride

Table 4.7 : Dissolved silica variation along Tambraparni estuary

Station No	Dissolved SiO_2 (mg/l)	(µmol/l)	Cl (mg/l)	TDS (mg/l)
Fresh				
1.	37	616.7	115	429
2.	40	666.7	165	487
3.	38	633.3	180	572
Saline				
4.	1.0	16.7	24,492	40,200
5.	Below Detection	0.0	27,991	40,600
6.	Below Detection	0.0	29,491	46,200

The silica values in µ moles/l are plotted against chloride (log scale) in Fig. 4.6. The theoretical dilution line has been drawn by joining points 1 and 6 which represent the lowest and are highest Cl values. It is clearly seen that in the fresh water (upper estuary) zone, SiO_2 is above the dilution line and falls sharply to near zero in the saline zone. This is in agreement with previous records of Bien et. al (1958) in the Mississippi estuary, Ray et. al. (1984) in the Mahanadi estuary and Ramanathan et. al. (1993) in the Cauvery estuary. These authors concluded that the rapid removal of silica is aided by flocculation of suspended material due to salinity. As discussed in Chapter 2, there is considerable difference in opinion as to whether biological uptake is important for this non-conservative behaviour of dissolved SiO_2. The suspended and bed load material collected at stations 4, 5 and 6 contained shell fragments but it

was not possible to distinguish any siliceous material of biological origin. On the other hand, the level of dissolved silica (around 40 mg/l) in the fresh water zone indicates that solubility of quartz and other cryptocrystalline silica minerals (which are abundant in the sediments) plays an important role. The same trend is seen in Figure 4.7, where dissolved silica is plotted against TDS (equivalent to salinity) separately for the fresh water and saline water zone.

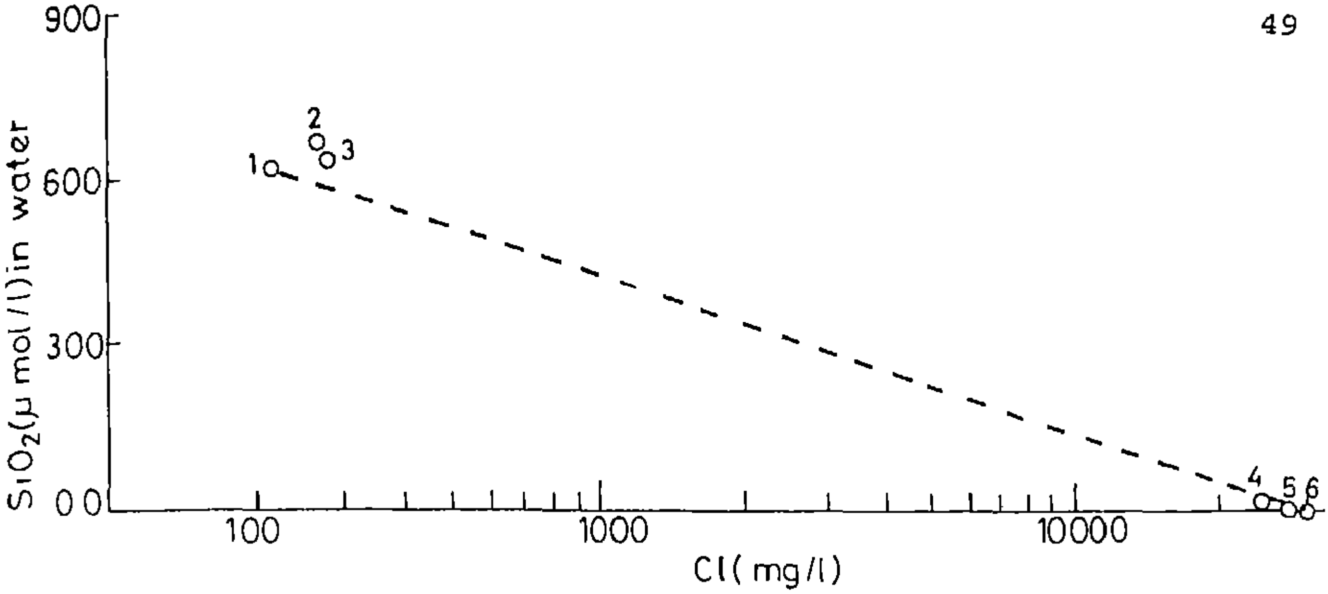
4.3.5 Phosphate in Water

In a manner similar to silica, dissolved phosphate values are listed along with Cl and TDS in Table 4.8. The symbol PO_4 stands for total orthophosphate species in solution.

Table 4.8 : Dissolved Phosphate variation in Tambraparni Estuary

Station	Dissolve PO_4		Cl	TDS
No.	(μg/l)	(μ mol/l)	(mg/l)	(mg/l)
Fresh				
1.	100	1.052	115	429
2.	50	0.525	165	487
3.	75	0.787	180	572
Saline				
4.	175	1.837	24,492	40,200
5.	100	1.052	27,991	40,600
6.	50	0.525	29,491	46,200

The plot of PO_4 in μ moles/l against Cl in log scale given in Fig 4.6 clearly shows the non-conservative behaviour of this



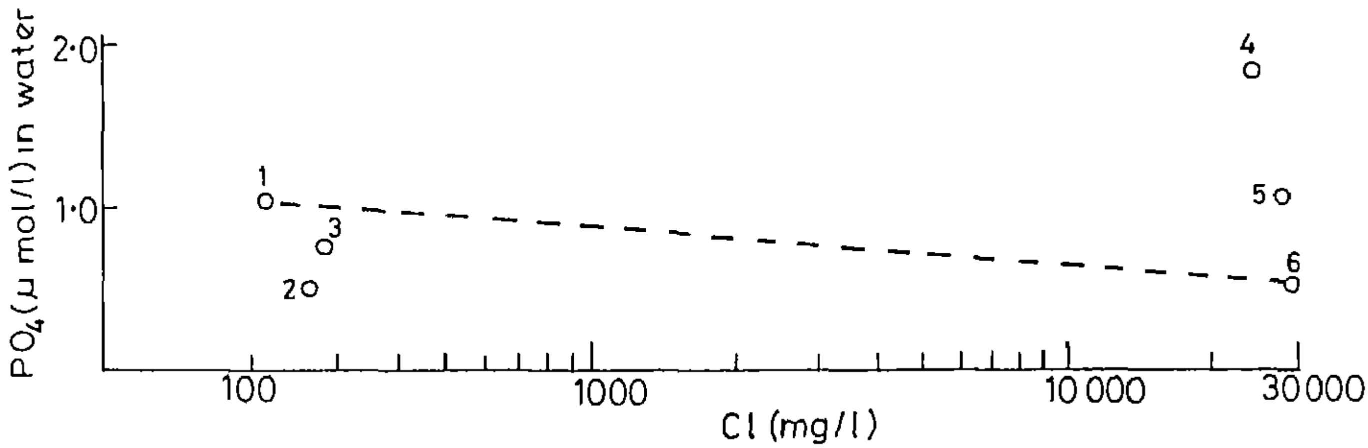


Fig.4.6: Variation of silica and phosphate with chloride

(Chloride in log-scale)

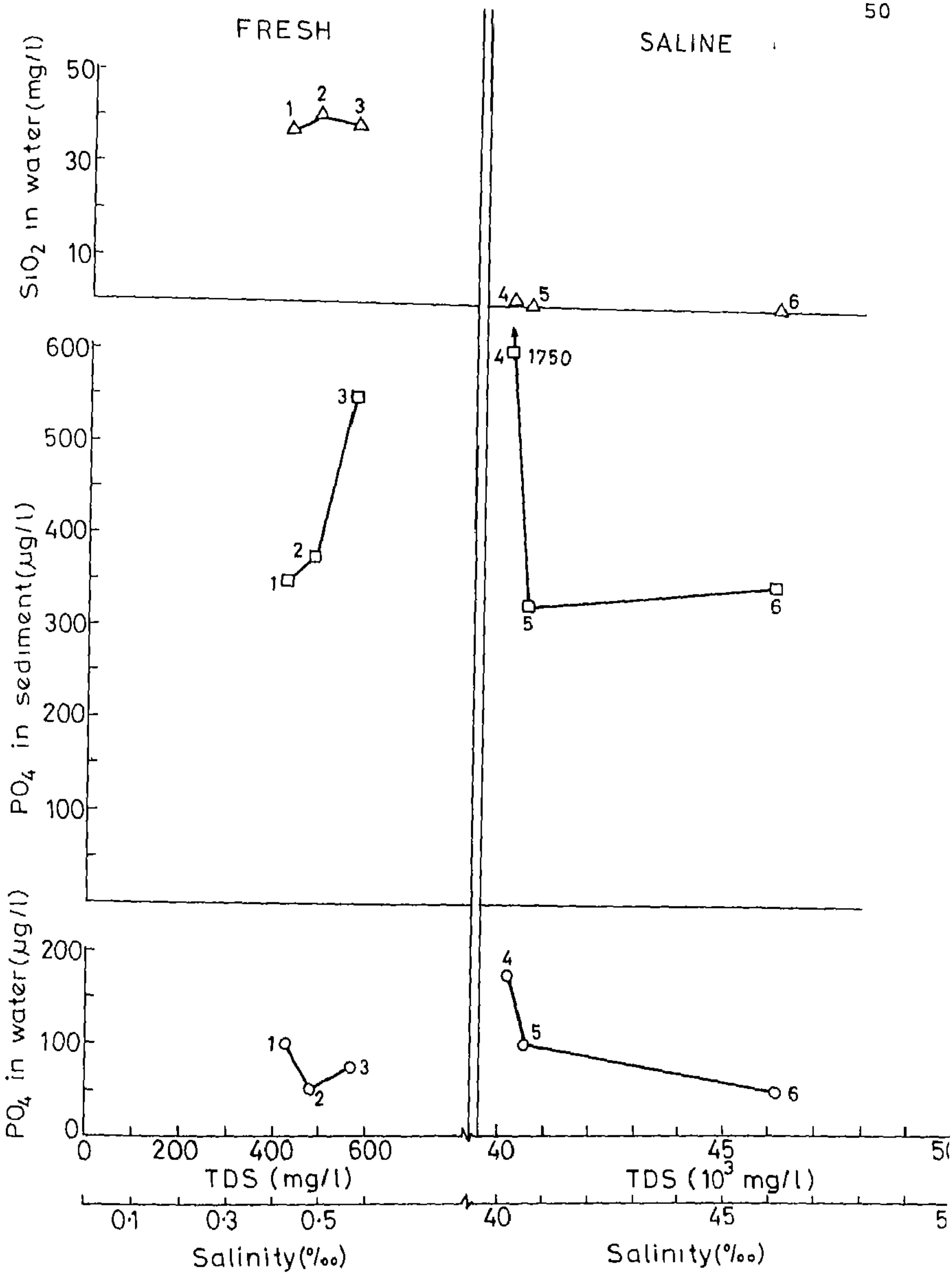


Fig.4.7: Variation of silica and phosphate with salinity

constituent because the values fall away from the Fig.4.7: theoretical dilution line between points 1 and 6. On the other hand, the pattern is opposite to that of silica in the sense that fresh water points are below and saline water points are above the line The most logical explanation is initial removal by suspended materials in the fresh water zone and desorption in the saline zone. As discussed in Chapter 2, earlier field and laboratory work in other estuaries have already identified this process (Upchurch et al., 1974; Maest et al., 1990; Raymahashay et al., 1990)

The source of phosphate is not definite but the nearby villages must be contributing from domestic and agricultural effluents. The anomalously high value at station 4 may be due to this factor. Several authors (Fox, 1990, Berner and Rao, 1993) have pointed out the role of iron oxides in phosphate adsorption In the Tambraparni river, occurrence of red coloured 'Teri' sand, iron coated quartz as well as jasper particles must be responsible for phosphate uptake. The decrease in phosphate between stations 5 and 6 (Fig. 4.7) may be due to biological uptake in highly saline water as suggested for silica earlier

4 4 Phosphate Extraction from Sediment

As discussed in Chapter 3, various methods are available to extract phosphate from soils and sediments by treating with single acids and mixture of acids with or without ashing at high temperature (Berner and Rao, 1993). However, the procedure adopted in the present work is essentially a modification of Jackson (1962) in which the 'dilute acid soluble phosphate' or 'available inorganic phosphate' is leached out in a mixture of

$HCl + H_2SO_4$. The results are listed in Table 4.9 along with PO_4, TDS and Cl values in corresponding water samples.

Table 4.9 : Phosphate Extracted from sediment

Station No.	PO_4 in Sediment ($\mu g/l$)	PO_4 in Water ($\mu g/l$)	Cl Water (mg/l)	TDS in Water (mg/l)
Fresh				
1.	350	100	115	429
2.	375	50	165	487
3.	550	75	180	572
Saline				
4.	1750	175	24,492	40,200
5.	325	100	27,991	40,600
6.	350	50	29,491	46,200

It is obvious that at each location, the fractionation of PO_4 is quantitatively in favour of the sediments. In other words, the sediments act as sink for phosphate. The value at Station 4, at the beginning of the estuarine mixing zone, is anomalously high together with a high value of dissolved phosphate. However, the general trend is that of removal from water between station 1 and 2 in the fresh water zone (Fig. 4.8) and corresponding increase in sediments. This is followed by a loss from sediment between station 4 and 6 and gain in water between stations 5 and 6, with an anomalous decrease in water between station 4 and 5. In other words, there is no direct correspondence between loss from sediment and gain in water as

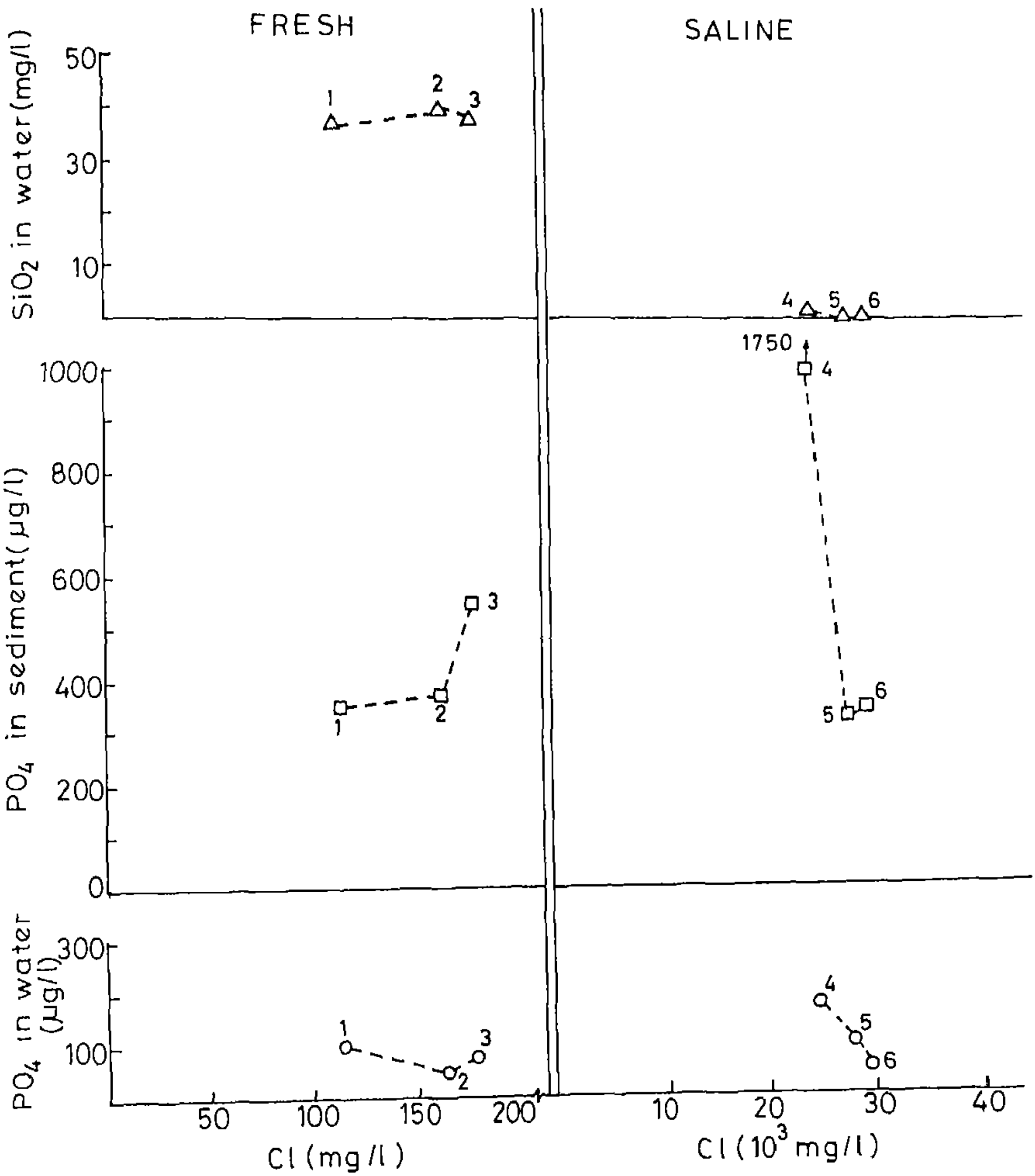


Fig.4.8: Variation of dissolved silica in water and dissolved phosphate in water and sediment with chloride in fresh and saline water zone

expected in an ideal situation. This is probably due to interference by periodic dissolution of shell fragments and biological uptake in the saline zone. The contribution of phosphate from the village of Attur and Punnakayal is also highly probable

CHAPTER 5

CONCLUSIONS

On the basis of field and experimental work described in earlier chapters, the following conclusions can be drawn:

1. The terrain occupied by the mouth of the Tambraparni river shows fluvial and aeolian landforms. The major fluvial land forms are flood plains and terraces. On the other hand, the main evidence of wind action is deposition of red sands (Teri sands) in dunes and ridges parallel to the coast. In the local geomorphological classification, the study area is within the Eastern Coastal Plains.

2. Predominance of unweathered minerals like quartz, felspar, sillimanite, garnet and pyroxene in the bed sediments indicates that the rate of transport of suspended material (mechanical weathering) exceeds the rate of chemical weathering and soil formation. Traces of poorly crystalline kaolinite was detected only in the flood plain deposits.

3. Dissolved silica and phosphate show non-conservative behaviour along the estuary. However, the trend of variation is different for these two constituents. For example, silica levels are high in the fresh water zone where chloride and TDS are relatively low. But the silica value quickly decreases to near zero level in the high-chloride, high-TDS saline zone. In contrast, dissolved phosphate shows an initial drop in the fresh water zone and an irregular increase in the saline zone. This is probably related to the adsorption by fresh water sediments and desorption in the presence of salinity as observed for several

estuaries by earlier workers. The role of biological processes in not confirmed.

4. Dilute acid soluble phosphate extracted from the sediments by an $HCl-H_2SO_4$ mixture showed an unsystematic variation with an apparent negative correlation with decrease or increase in phosphate dissolved in water.

5. Some of the discrepancies from an ideal trend is obviously due to the contribution of domestic and agricultural waste from nearby villages. However, detailed sampling is required to verify this possibility.

Suggestions for Future Work

1. Effect of seasonal changes on both sediment and water characteristics should be verified.
2. More closely spaced sampling stations should be selected in both the fresh water and saline zones to confirm the geological and geochemical parameters established during this work.
3. The effect of organic matter on phosphate adsorption-desorption can be verified by repeating the laboratory experiments before and after removal of organic constituents from sediments by chemical treatment.
4. Phosphate available from sediments can be further classified into organic phosphate, inorganic phosphate and phosphate associated with iron minerals as suggested by Berner and Rao (1994).

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